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APPLICATION FOR UNITED STATES LETTERS PATENT

Title:

PHOTORESIST COMPOSITION

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PHOTORESIST COMPOSITION

BACKGROUND OF THE INVENTION

Technical Field

A photoresist composition having a low light absorbance to a light source of a

5   wavelength of less than 200 nm is disclosed. More specifically, a VUV (vacuum

ultraviolet) photoresist composition comprising TIMD (tetraisopropyl methylene

diphosphonate) is disclosed that lowers a light absorbance to a light source of a

wavelength of 157 nm.

Description of the Related Art

10   A photoresist composition used for a VUV photoresist film needs to have a low

light absorbance at a wavelength of 157 nm, an excellent etching resistance, an ability

to be adhesively attached to a wafer, and an ability to be developed with standard 2.38

wt% or 2.6 wt% aqueous TMAH (tetramethylammonium hydroxide) solutions.

Recently, much research has been conducted on resins having a high

15   transparency at a wavelength of 193 nm and the same etching resistance as that of

novolack resin which is a photoresist resin for KrF. However, since most of these

photoresist resins show a high light absorbance at a wavelength of 157 nm, these

photoresist resins are not suitable for a VUV photoresist film.

In order to overcome the above-described problem, research on a photoresist

20   resin containing fluorine and silicon has been conducted. Unfortunately, polyethylene

or polyacrylate resins containing fluorine have weak etching resistance, low solubility

in the TMAH aqueous solution which results in degradation in development of the

photoresist film, and poor adhesive property to a silicon substrate. Additionally, the

compounds containing fluorine are gaseous at room temperature due to their low

25   boiling point, and they should be handled with care because of their strong toxicity.

On the other hand, photoresist resins containing silicon have an etching process

which is required to have the two-step treatment with hydrofluoric acid-oxygen. It is

therefore difficult to completely remove fluorine after the treatment process.

In addition, photoresist resins containing silicon have an outgassing

30   phenomenon where gas is generated in an exposure process, thereby damaging lens of a

scanner or a stepper. In other words, silicon gasified by the exposure reacts with air to

be transformed into SiO_2. When the SiO_2 is deposited on lens, a method for removing

the SiO_2 has not been suggested yet, and expensive lens of the scanner or the stepper

must be replaced frequently.

Although polyethylene or polyacrylate resins containing fluorine having excellent solubility to developing solution may be used for VUV photoresist films, these resins still have poor etching resistance and adhesive property to a substrate, and high light absorbance.

SUMMARY OF THE DISCLOSURE

Accordingly, a light absorption depressant which lowers a light absorbance of photoresist at a wavelength of less than 200 nm, and a photoresist composition containing the same are disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph illustrating the experimental results of Example 1 and Comparative Example 1.

Fig. 2 is a graph illustrating the experimental result of Example 2.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

TIMD (tetraisoprophyl methylene diphosphonate) as a light absorption depressant, and a photoresist composition containing the same are disclosed.

There is provided TIMD compound represented by Formula 1 which lowers light absorbance to a light source of a wavelength of less than 200nm.

Formula 1
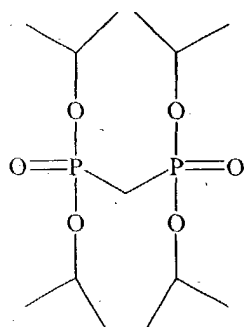
There is also provided a photoresist composition comprising the TIMD compound.

Preferably, the TIMD is present in an amount ranging from 0.01 to 25 wt%, more preferably ranging from 0.01 to 20 wt% based on a base resin included in the photoresist composition.

Although the photoresist composition is more useful in a photolithography process of a wavelength of 157 nm, it is also useful in a photolithography process of a wavelength of less than 200 nm such as 193 nm.

An employable base resin in this disclosure is not specifically limited. Referring to the following Examples 1 and 2, it is understood that desirable results are obtained when the disclosed light absorption depressant is added in the photoresist composition comprising different materials as base resin such as (1) a poly(norbornene hexafluoroalcohol) represented by Formula 2 or (2) a blend polymer of polymers represented by Formula 3a and Formula 3b.
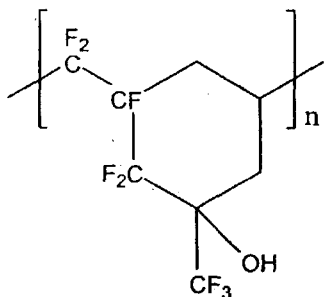
Formula 2
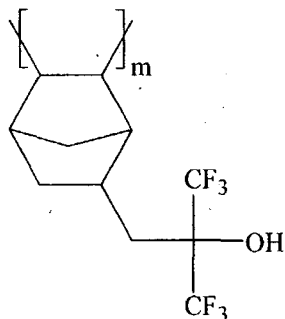
Formula 3a
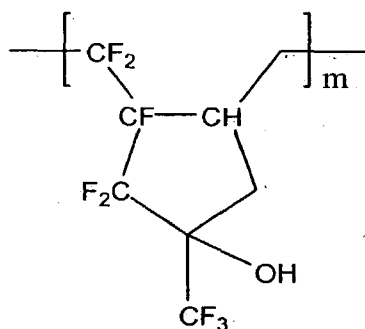
Formula 3b

It is preferable that the photoresist composition containing the disclosed light absorption depressant is a chemically amplified photoresist composition containing a photoacid generator. As the photoacid generator, any compound that can generate acid when exposed to light can be employed.

A process for forming a photoresist pattern comprises:

(a) coating a photoresist composition described above on an underlying layer to

form a photoresist film;

(b) baking the photoresist film, and then exposing the baked photoresist film to light;

(c) baking the exposed photoresist film; and

(d) developing the baked photoresist film to obtain a photoresist pattern.

There is also provided a semiconductor device manufactured according to the above-described process.

In addition, a photoresist composition comprising a hydrocarbon compound including a P=O group is disclosed.

The disclosed photoresist composition will be described in more details by referring to examples below, which are not intended to be limiting.

Example 1. Variation of light absorbance depending on the added amount of TIMD (1)

Poly(norbornenehexafluoroalcohol) of the above Formula 2 which is photoresist polymer for 157 nm was mixed with TIMD as an addtive in an amount ranging from 0 to 20 wt%. Then, the resultant was coated on a substrate at a thickness of 2000 Å to form a thin photoresist film.

Next, the light absorbance of the thin film measured using an ellipsometer of Sematech was shown in Table 1 and Fig. 1. The light absorbance was obtained by calculating light absorbance to the thin film having a thickness of 2000 Å in terms of a value to the thickness of 1 μm. The value of α10 to a light source of 157.6 nm was shown in Fig. 1.

Table 1

Amount of added TIMD (%)	n (157.6nm)	k (157.6nm)	$\alpha(\mu m^{-1})$ (157.6nm)	α_{10} (157.6nm)	$\alpha(\mu m^{-1})$ (193nm)	α_{10} (193nm)
0	1.667	0.049	3.87	1.68	0.25	0.107
5	1.667	0.046	3.70	1.61	-	-
10	1.687	0.045	3.56	1.55	0.19	0.085
20	1.702	0.042	3.35	1.45	0.10	0.044

n: refraction index
k: light absorption coefficient
$\alpha(\mu m^{-1})$: light absorbance of material when light of a predetermined wavelength is penetrated into the material at a thickness of 1 μm
$\alpha_{10} \times 2.3 = \alpha(\mu m^{-1})$

Example 2. Variation of light absorbance depending on the amount of added TIMD (2)

The blend polymer of Formula 3a and 3b which is photoresist polymer for 157 nm were mixed with TIMD as an addtive in an amount ranging from 0 to 20 wt%. Then, the resultant was coated on a substrate at a thickness of 2000 Å to form a thin photoresist film.

Next, the light absorbance of the thin film measured using an ellipsometer of Sematech was shown in Table 2 and Fig. 2. The light absorbance was obtained by calculating light absorbance to the thin film having a thickness of 2000 Å in terms of a value to the thickness of 1 μm. The value of α10 to a light source of 157.6 nm was shown in Fig. 2.

Table 2

Amount of added TIMD (%)	n (157.6nm)	k (157.6nm)	$\alpha(\mu m^{-1})$ (157.6nm)	α_{10} (157.6nm)	$\alpha(\mu m^{-1})$ (193nm)	α_{10} (193nm)
0	1.553	0.019	1.52	0.66	0.32	0.139
5	1.580	0.012	0.99	0.43	-	-
10	1.573	0.013	0.99	0.43	0.23	0.098
15	1.591	0.011	0.88	0.38	-	-
20	1.612	0.011	0.88	0.38	0.12	0.053

n: refraction index
k: light absorption coefficient
$\alpha(\mu m^{-1})$: light absorbance of material when light of a predetermined wavelength is penetrated into the material at a thickness of 1 μm
$\alpha_{10} \times 2.3 = \alpha(\mu m^{-1})$

Comparative Example 1. Variation of light absorbance in other additives

The procedure of Example 1 was repeated using 2-methyl-hexfluoro isopropoxy ethoxy methane represented by Formula 4 instead of the TIMD as an additive. The experimental result was shown in Table 3 and Fig. 1. The value of α10 to a light source of 157.6 nm was shown in Fig. 3.
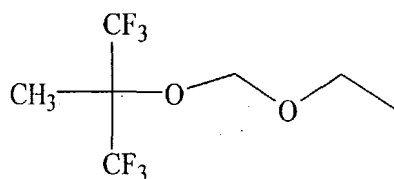
Formula 4

$$CH_3 - \underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}} - O \diagup\diagdown O \diagup\diagdown$$

Table 3

Amount of added additive (%)	n (157.6nm)	k (157.6nm)	$\alpha(\mu m^{-1})$ (157.6nm)	α_{10} (157.6nm)
0	1.668	0.049	3.87	1.68
5	1.665	0.047	3.74	1.62
10	1.666	0.047	3.74	1.63
20	1.666	0.046	3.66	1.59
n: refraction index k: light absorption coefficient $\alpha(\mu m^{-1})$: light absorbance of material when light of a predetermined wavelength is penetrated into the material at a thickness of 1μm $\alpha_{10} \times 2.3 = \alpha(\mu m{-}1)$				

As shown in Examples 1 and 2 and the Comparative Example, the disclosed TIMD more remarkably reduces the light absorbance (α10) than the same amount of the compound of Formula 4 which has been conventionally used to lower light absorbance of a photoresist polymer. When different kinds of photoresist polymers are individually used, the light absorbance of each polymer is also shown to be reduced. Additionally, since the light absorbance is reduced in a wavelength of 193 nm as well as of 157 nm, the disclosed TIMD is useful in a photolithography process using an ArF(193 nm) as well as a VUV(157 nm).

Meanwhile, it is presumed that a P=O group included in the TIMD compound may remarkable reduce the light absorbance. The similar effect may be obtained when a compound including a P=O group is added in a photoresist composition instead of the TIMD compound. In addition, the light absorbance of photoresist may be reduced when a predetermined amount of a P=O group is included in a photoresist composition, regardless of the position of the P=O group. For example, the light absorbance of photoresist may be lowered if a P=O group is introduced into a base resin of a photoresist composition or included in a dissolution inhibitor.

As discussed earlier, light absorbances of photoresist materials to light sources of 157 nm and 193 nm are remarkably reduced when a TIMD compound is added as an additive in a conventional chemically amplified photoresist composition. Instead of the

TIMD compound, a compound including a P=O group may have the similar effect to the TIMD. Accordingly, it is expected that the light absorbance of photoresist may be also reduced by introducing a P=O group into a base resin.